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Title: Improved Method to Coat or Finish Sheet Materials Using Aqueous Dispersions of Polyurethanes

### **Improved Method for Coating or Finishing Sheet Materials Using Aqueous Dispersions of Polyurethanes**

The coatings or finishes applied on sheet materials such as natural or synthetic leather must present good aesthetic qualities and exhibit good abrasion resistance and good flexural properties under repeated tension or bending and this is difficult to achieve because these two properties have a tendency to be mutually exclusive. Particularly, no one has been able to obtain the desired results using aqueous coating compositions.

The Applicant has found that it is possible to obtain coatings exhibiting excellent bending and abrasion resistance for coating or finishing natural or synthetic leather using mixtures of aqueous dispersions of cationic polyurethanes, hardeners based on aqueous solutions of methylolmelamine compounds having on average at least 3 methylol groups which could be etherified with lower aliphatic monoalcohols and acids or acid reaction compounds, the relative proportions by weight of polyurethane and hardener in the mixture being comprised between 100:25 and 100:100, preferably between 100:35 and 100:60 dry materials.

The polyurethanes suitable for the preparation of aqueous dispersions of polyurethanes used in the method of the invention are products derived from the usual high molecular weight compounds such as polyesters, polyesteramides, polyethers bearing terminal hydroxyl or polyisocyanate groups and if desired chain extending agents containing quaternary ammonium groups.

These polyurethanes must exhibit a certain hydrophilicity and particularly, the capacity to form aqueous dispersions or opaque colloidal solutions of molecular associations without using emulsifiers or wetting agents.

For example, cationic polyurethanes of this type are obtained by using a compound containing at least basic tertiary nitrogen atoms in the synthesis of the polyurethane and reacting the resulting polyurethane, containing the basic tertiary nitrogen atoms, with alkylating agents and/or organic or mineral acids. The position of the basic nitrogen atoms in the polyurethane molecule is not important. Additionally, we can start with polyurethanes bearing reactive halogen atoms that are capable of quaternizing and that react with tertiary amines. The polyurethanes can also be prepared by a procedure that calls for a quaternization that produces the elongation of the chains, for example, by preparing dihalide urethanes from compounds bearing two isocyanate groups and halogenated alcohols and by reacting these dihalourethanes with ditertiary amines. Conversely, ditertiary diaminourethanes can be prepared from compounds bearing two

isocyanate groups and tertiary amino alcohols and then reacting these diaminourethanes with reactive dihalogenated compounds.

Cationic polyurethanes can naturally also be prepared from a saline type cationic starting compound such as a quaternized basic polyether or an isocyanate containing quaternary nitrogen atoms. These known procedures have been described, for example, in French Patent number 1, 379,133 or Belgian Patent number 639,107, French Patent number 1,383,252 or Belgian Patent number 640,789, Belgian Patent 653, 223, French Patent 1,416,463, Belgian Patent 658,026, French Patent 1,423,157, Belgian Patent 636,799 or French Patent 1,386,247.

Naturally, the polyurethane mass can also contain urea groups in addition to urethane groups. If it is desired to obtain a final product with satisfactory properties the number of urethane groups and optional urea groups in the polyurethane mass must represent approximately 8 to 35% of the weight of the latter.

The quaternary ammonium groups must represent approximately 0.1 to 1.5% of the polyurethane mass. The products exhibiting a lower salt content are less suitable because they produce dispersions where the particles are much larger or films that are softer. The products containing more than 1.5% quaternary ammonium groups are not suitable because of their strong hydrophilic properties.

Depending on the chemical composition and preparation conditions, we can obtain colloidal aqueous solutions or aqueous dispersions having a particle size ranging between 50 and 1,000 millimicrons. The particle size depends particularly on the number of quaternary ammonium groups present.

For the implementation of the method according to the invention, we preferentially use polyurethanes that are prepared from high molecular weight polyhydroxylated compounds (from 500 to 5,000), polyisocyanates, a chain extender such as N-methyl-diethanolamine and when desired, other non-basic chain extenders such as diols, diamines, water and optionally substituted hydrazines. The polyurethane mass has a predominantly linear structure that is soluble in organic solvents, preferably containing from 1 to 12% N-methyldiethanolamine, 10 to 60% of the tertiary nitrogen introduced in this manner into the polyurethane mass are quaternized by an alkylating agent such as dimethyl sulfate, ethyloxide, chloromethyloxide, diethyl sulfate or bromoethanol; 30 to 70% of this tertiary nitrogen is neutralized with an acid such as hydrochloric acid, lactic acid or acetic acid in the presence of water. When di- or polyfunctional alkylating agents are used, 5 to 20% of the tertiary nitrogen is not converted, in general, into saline groups.

It is advantageous to use, partly at least, di- or tri-functional alkylating agents such as 1,4-dibromobutane, 3-xylylene dichloride, 1,3-dimethyl-4,6-bis-chloromethylbenzene, methylene-bis-bromacetamide, trimethylol propane tris-chloroacetate and di- or trifunctional acids exhibiting a pH value below 4 such as phosphoric acid, oxalic acid or sulfuric acid as aqueous solutions. These reactants first react as monofunctional compounds or predominantly monofunctional and act as crosslinking agents. The dispersed polyurethanes can naturally also be a methylolether group introduced, for example, for subsequent crosslinking.

The colloidal solutions or dispersions free from organic solvents are prepared with a solids content comprised, for example, between 30 and 65%.

The hardeners or curing agents used are tri-, tetra-, penta- or hexamethylolmelamine, alone or as mixtures that can be obtained by the traditional methods and that can be etherified with three moles or more and preferably an average of 3 or 6 moles of a lower aliphatic monoalcohol. Suitable alcohols, for example, include ethanol or more particularly, methanol. The products obtained are hardeners or curing agents that are commercially available. We can also use polycyclic condensates of melamine formaldehyde such as methylol derivatives of methylene-bis-melamine and its ethers.

The hardeners are added to this polyurethane dispersion before application. The amounts used range from 25 to 100 parts, preferably, from 30 to 55 parts per 100 parts of solid polyurethane based on dry weight content. Commercially available aqueous solutions of hardeners typically have concentrations between 40 and 50% but it is perfectly possible to see higher concentrations, or when necessary, dilute the polyurethane dispersion before mixing. Generally, the hardener solutions have pH values ranging from 5 to 7. If the hardener is not compatible with the polyurethane latex, this incompatibility can be corrected by adjusting the pH between the limits of 4 and 7. It is often advantageous to apply over natural or synthetic leather, before the final finish, an under layer containing, for example, from 30 to 40 parts hardener per 100 parts polyurethane. The final layer finish contains, for example, 40 to 60 parts hardener.

In order to accelerate the curing or setting of the coating, we can add to the polyurethane mixture and the hardener, acids or compounds with an acid reaction. Suitable acids include hydrochloric acid, sulfuric, phosphoric, tartaric, oxalic, citric, lactic, salicylic and most particularly, maleic acid. Suitable salts with an acid reaction include ammonium chloride and diammonium phosphate. The amounts of these additives can range within broad limits. In most cases, 0.5 to 3% is used based on the total amount of polyurethane and curing agent, dry weight, however, strong acids can be used in small quantities and weak acids or the salts of weak acids in high amounts. However, for practical and commercial reasons, these amounts should not exceed 50%. If the polyurethane dispersions themselves have a pH below 6 and especially below 5, and in other words, if they already exhibit some acidity, it often serves no useful purpose to add more acid.

The coating mixtures containing the polyurethane dispersion, the curing solution and the acid catalyst could also contain pigments, colorants, stabilizers, other polymer dispersions, wetting agents, emulsifiers, light protection agents, opacifiers, fillers, oils, waxes and dispersions of organic liquids such as petroleum hydrocarbons, as well as additives to improve the product gloss.

The solids content of the mixture can vary within a broad range depending on the application but generally the range is comprised between 10 and 50%.

The mixture is applied to a support using the traditional techniques such as spraying, printing, casting, blade stripping or a combination of these techniques. The best way to achieve a good water vapor permeability consists in spraying or printing using network or system application devices. The amounts applied can represent, for example, from 1 to 50 g, preferably from 10 to 30 g of solids per m<sup>2</sup> of surface.

After the application, the coating is dried and heated. The higher the temperature, the faster the heating. However the temperature observed must be lower than the softening temperature of the

finish and of the support. Generally, we operate at temperatures comprised between 80 and 160°C, and in most cases, temperatures of 100 to 140°C are sufficient. The duration of the heating process is then 60 to 3 minutes, for example. The hardening or curing continues after heating so that the coating layer does not acquire its final properties until 1 to 10 days had elapsed.

The mixture of the invention is suitable particularly for the application of finishes over synthetic leather, for example, over a microporous sheet that can be obtained by known techniques such as coagulation or evaporation starting from polyurethanes or polyvinyl compounds or combinations of products among others by the method described in Belgian patent 692,116, French patent 1,510,261, Belgian patent 700,304 or in French patent 1,529,109.

After drying and heating, the finishes can be pressed, laminated, hot stamped or embossed.

The following examples illustrate the invention without limiting its scope. In these examples, the parts and percent refer to weight unless otherwise indicated.

#### EXAMPLE 1

We react 1000 g of polyester with an OH (hydroxyl) index of 63 prepared from phthalic acid, adipic acid and ethylene glycol (molar ratio 1:1:2.2) with 190.5 g of toluene diisocyanate (mixture of two isomers at a 65:35 ratio) at 100°C or 1 hour and 30 minutes. Then 624 ml of acetone and 52 g of N-methyldiethanolamine are added. The reaction mixture is agitated for 1 hour and 40 minutes at 70°C; 340 ml of acetone is added and agitated for another hour at 70°C. We then add a 20 g solution of 1,3-dimethyl-4,6-bis-chloromethylbenzene in 680 ml of acetone. 60 minutes later we introduce successively under agitation, 2 g of dibutylamine in 10 ml of acetone, 7.2 ml of 85% phosphoric acid in 120 ml in water and 1100 ml of water at a temperature of 70°C. The acetone is distilled under the water trap vacuum. A very fluid latex is obtained with fine particles and 52% solids.

#### EXAMPLE 2

The operating procedure is the same as in the preceding example except that 1,3-dimethyl-2,6-bis-chloromethylbenzene is replaced by 17.3 g of p-xylylene dichloride. We obtained a very fluid latex with larger particles and 52% solids.

#### EXAMPLE 3

The operating procedure is the same as in the previous example except that we use 1000 g of a polyester with a OH index of 68 prepared from adipic acid, hexanediol and neopentyl glycol (in 15:11:6 proportions), 218 of toluene diisocyanate (isomer mixture with a 65:35 ratio), 64 g of N-methyldiethanolamine, 30.5 g of 1,3-dimethyl-4,6-bis-chloromethylbenzene, 2 g of dibutylamine, 7.2 ml of 85% phosphoric acid and 1150 ml of water. We obtained a milky white latex that is very fluid with 56% solids.

#### EXAMPLE 4

The operating procedure is the same as in example 1 but we use 173 g of toluene diisocyanate, 40 g of N-methyldiethanolamine, 10 g of 1,3-dimethyl-4,6-bis-chloromethylbenzene, 6.0 ml of 85% phosphoric acid and 2.0 ml of acetic acid. We obtained a very fluid latex and largely dispersed with 45.5% solids.

#### EXAMPLE 5

The operating procedure is the same as in example 1 but we use 173 g of toluene diisocyanate, 40 g of N-methyldiethanolamine, 8.6 g of p-xylylenedichloride, 6.0 ml of 85% phosphoric acid and 4.0 ml of acetic acid. The latex obtained is very fluid, largely dispersed with 50% solids.

#### EXAMPLE 6

We dissolve 1000 g of the polyester used in Example 3 in 200 ml of acetone at 40°C. We then add to it the adduct of 24 g of N-methyldiethanolamine and 84.6 g of 1,6-hexane diisocyanate in 50 ml of acetone. We then add 143 g of toluene diisocyanate (mixture of two isomers in a 65:35 ratio) and 20 g of 1,3-dimethyl-4,6-bis-chloromethylbenzene. The reaction mixture is agitated for 3 hours at 60°C and it is allowed to stand overnight at room temperature. The viscous reaction product is diluted with 1.1 liter of acetone and we add 39 ml of ethylenediamine in 200 ml of acetone. After a few minutes the solution becomes very viscous. We then introduce under agitation 12 ml of acetic acid in 60 ml of water, then 2 liters of water. After removing the acetone by distillation, we obtained a very fluid dispersion containing 45% solids.

#### EXAMPLE 7

500 g of the polyester used in example 1 is agitated with 92 g of hexane 1,6-diisocyanate for 3 hours at 130°C. We then finish as described in example 1. We obtained a very fluid latex containing 35% solids. The examples below illustrate more precisely the embodiments of the method according to the invention.

#### EXAMPLE 8

We mix 200 parts of a 58% polyurethane dispersion obtained as described in example 1 with a mixture of 120 parts of a 52% aqueous solution of hexamethyl hexamethylolmelamine ether, 3.5 parts of maleic acid in 630 parts water and 50 parts of a commercial black pigment in an aqueous medium and containing an emulsifying agent with a carbon black content of approximately 40%. This mixture is sprayed very finely and uniformly over the microporous polyurethane synthetic leather using a spray nozzle as practiced in prior art at an application rate of 15 to 20 g solids per m<sup>2</sup> of synthetic leather surface. The coated surface is dried at 60°C for 5 to 6 minutes and then, it is taken for 20 minutes to 70°C and it is heated for 15 minutes at 140°C. After 3 days, the finish exhibits a water vapor permeability of 6 mg/cm<sup>2</sup>/hour (measurement carried out according to what is stated in IUP Standard 15; "Das Leder", 1961, 86-88), a bending flexibility exceeds 100,000 flexions (unit of measurement carried out with a flexometer, Standard IUP 20; "Das Leder", 1964, 87-88) and a strong abrasion resistance (measurement conducted according to SATRA: J. Soc. Leather Trades Chem, 1957, 120-125). If maleic acid is not used, the abrasion resistance is lower. When the finish is cured in the presence of maleic acid at 110°C instead of 140°C, the abrasion resistance and the folding/bending endurance are much lower. In the absence of the curing agent the finish obtained exhibits an unacceptable flexural and abrasion

resistance. When the melamine derivative mentioned above is replaced with equivalent amounts of formaldehyde, paraformaldehyde, dimethylolpropylene urea or dimethylolethylene urea the abrasion resistance is insufficient and with formaldehyde, the product has insufficient abrasion resistance and in the case of formaldehyde, the product exhibits an insufficient flexural resistance.

#### EXAMPLE 9

We dissolved 175 parts of a 45% aqueous solution of trimethyl trimethylolmelamine ether in 535 parts water and the mixture is agitated with 4 parts of maleic acid in 250 parts of the polyurethane dispersion from example 8. We then add 40 parts of the black pigment-paste used in example 8. We apply this mixture with a 4 way spraying equipment over a microporous polyurethane synthetic leather that is then dried for 5 minutes at 70°C, pressed for 1 second at 100°C and finished by a curing of the finish at 125°C over 20 minutes. The final finish exhibits good flexural endurance and abrasion resistance and its water vapor permeability exceeds 2 mg/cm<sup>2</sup>/hour.

We obtained a similar result when the experiment is repeated with 145 parts of a melamine derivative solution. The coating exhibits a lower abrasion resistance and a lower flexural endurance when 88 parts of the curing solution are used.

#### EXAMPLES 10 to 15

The conditions observed and the results obtained in these examples are reported in the attached table.

### **CLAIMS**

1. An improved method for coating or finishing sheet materials such as natural or artificial leather by applying a dispersion of a synthetic polymer, a curing agent and an acid or acid reaction catalyst, characterized in that it uses an aqueous dispersion of a cationic polyurethane as a polymer dispersion and an aqueous solution of a methylolmelamine compound exhibiting an average of at least 3 methylol groups able to be etherified by lower aliphatic monoalcohols as the curing agents with relative proportions by weight of polyurethane/curing agent of 100:25 to 100:100 based on dry weight.
2. Method according to claim 1 where the cationic polyurethane contains 0.1 to 1.5% quaternary ammonium groups.
3. Method according to claim 1, where the polyurethane dispersion particles have a dimension comprised between 50 and 1000 millimicrons.

TABLE

Example number	polyurethane dispersion	hardener	acid	pigment	water
10	25 parts of P II at 52%	6 parts of HMH	0.35 parts of MA	4 parts	65 parts
10a	25 " " P II at 52%	12 " " HMH	0.35 " " MA	4 "	59 "
11	25 " " P III at 56%	12.5 " " TMT	0.4 " " MA	4 "	58.5 "
12	31 " " P IV at 45.5%	15.5 " " TMT	4 " " Am 10%	5 "	44.5 "
13	28 " " P V at 50%	15.5 " " TMT	4 " " MA 10%	5 "	47.5 "
14	33 " " P VI at 43%	15.5 " " TMT	0.5 " " MA	5 "	46 "
15	40 " " P VII at 35%	15.5 " " TMT	0.5 " " MA	5 "	39 "

The abbreviations used in the table above have the following meanings:

P II, III, etc: polyurethane from example 2, example 3, etc; MA: maleic acid; Am: 10% ammonium chloride solution; TMT: trimethyl trimethylolmelamine ether, 45% aqueous solution; HMH: hexamethyl hexamethylolmelamine ether, 52% aqueous solution. In example 13, the maleic acid is added last as a 10% solution; generally, the mixture is prepared as in example 8.

In all examples, we obtained an abrasion resistance and a bending endurance that is very superior to those obtained in the comparative experiments carried out with no hardener or acid catalyst.